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Dispersion and Slip Casting of Hydroxyapatite

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The dispersibility in deionized water of hydroxyapatite (HA) synthesized by a high-temperature (1000°C) solid-state reaction between tricalcium phosphate and calcium hydroxide was investigated as a function of the pH of the medium and the quantity of two dispersing agents (A = inorganic, B = organic) added to the slips. Although pH modification had a negligible effect on dispersibility, both of the dispersing agents produced a good dispersion at considerably higher concentrations (>2 wt% of HA). At optimum amounts (2–4 wt%) of the dispersing agents, the slips showed near-Newtonian flow behavior up to 45 wt% solids loading and non-Newtonian behavior at >50 wt%. By the optimal addition of dispersing agents and conditioning by ball milling, 60–67 wt% (32–39 vol%) solids-loaded HA slips could be cast into plaster molds to produce 50%–58% dense green bodies, which, in turn, sintered to 90%–94% density in the temperature range 1300°–1400°C. The sintered HA exhibited a three-point flexural strength of 40–60 MPa and a homogeneous microstructure, with interspersed microporosities.

I. Introduction

SLIP CASTING as a shaping/forming process for both clay- and nonclay-based ceramic products has had a very long history.[1,2] Since its origin, the process has emerged as one of the major forming techniques for large-scale fabrication of both monolithic and composite ceramic components having either simple or complicated shapes.[3,4] Further, the colloidal processing methods that influence the deflocculation and stabilization behavior of powder particle dispersions in a liquid medium, either by manipulation of electrostatic surface charges on the powder particles or by a process of separation of individual particles by adsorption of a long chain polymer (steric separation) or polyelectrolytes (electrosteric separation) onto the particle surface, have been established recently.[5,6] The colloidal dispersion methods enable a control over packing density variations in a green compact and, thereby, the development of desired microstructures in the sintered product.

Synthetic hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$), because of its biocompatibility and chemical and biological affinity with bone tissues, has potential applications as a bioceramic material.[7–12] Even though synthetic HA ceramics have been studied extensively during the past two decades, very little information is available in the literature[10,12] on the methods of processing such ceramics. In most of the studies, only conventional dry powder compaction, followed by sintering, has been used as a processing route for HA ceramics. Only very recently has the use of colloidal consolidation techniques been adapted for the processing of HA ceramics.[13–19]

Galassi *et al.*[13] studied slip casting of a commercial HA and reported that the method is suitable for forming a high-density body. Nordstrom and Karlsson[14] found slip casting of the commercial HA powder difficult, because of the lower zeta potential values for the slip. However, those researchers were able to successfully slip cast a well-dispersed slip consisting of a mixture of commercially available tricalcium phosphate (TCP) and calcium hydroxide ($Ca(OH)_2$) containing nonionic deflocculants, and they vacuum-sintered such cast bodies to near the theoretical density of HA. Toriyama *et al.*[15] investigated the dispersion behavior of mechanochemically synthesized HA powders in water, using various dispersing agents. They observed that, although pH modification had a negligible effect, anionic polyelectrolytes at considerably higher concentrations (≥3 wt%) effectively stabilized the suspensions through an electrosteric mechanism. The significant improvement in mechanical properties achieved for slip-cast samples, as compared with those for cold-pressed samples, proved the importance and relevance of the colloidal approach for consolidation of fine HA powders. Lelievre *et al.*[16] found that, from among various dispersing agents (anionic, cationic, and nonionic) for HA, anionic polyelectrolytes were the most efficient. Such a suspension, solids-loaded to 73 wt% with a precipitated and calcined (at 800°–900°C) HA powder, was slip cast and sintered to a density >96%. The calcination temperature affected both the morphology and the chemical nature of the surface of the particles, with the optimum calcination temperature >800°C. Arita *et al.*[17] prepared HA ceramic sheets with widely ranging porosities (62% maximum) through tape casting a nonaqueous slurry of a mixture of dicalcium phosphate ($CaHPO_4$) and calcium carbonate ($CaCO_3$) powders, followed by their sintering at high temperatures. Very recently, Liu[18] fabricated a porous HA bioceramic by casting an HA slip containing polymeric powder as a pore former. Terpstra *et al.*[19] studied the colloidal stability of commercial HA powder and its calcined version as a function of pH and deflocculant concentration. Those researchers slip cast high solids-loaded slips, which sintered to ≥99% of theoretical density.

The present study is aimed at investigating the optimization of an aqueous dispersion of HA powder synthesized by solid-state reaction, and its slip casting and sintering, followed by characterizing the sintered product.

II. Experimental Procedure

(1) HA Powder Preparation

The HA powder used in this study was synthesized in the laboratory[20] by a solid-state reaction between commercially available TCP powder (Rolex, Mumbai, India) and $Ca(OH)_2$ (S. D. Fine Chemicals, Ltd., Boisar, India). The starting TCP and $Ca(OH)_2$ powders were mixed in the molar ratio 3:2 by wet milling in polyethylene jars, using alumina balls as milling media, for 12–16 h, and the resulting slip was cast into plaster molds. The dried samples were heat-treated at 1000°C for 8 h in an SiC furnace (Heat Kiln Industries, Bangalore, India). The HA powder so produced was characterized by X-ray diffractometry (XRD; Model PM 9002, Philips Research Laboratories, Eindhoven, The Netherlands) and infrared (IR) spectroscopy (Model 682, PerkinElmer, Inc., Norwalk, CT).

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(2) Preparation and Characterization of HA Slip

The slips were prepared by dispersing HA powder in deionized water, using magnetic stirring, for 10–20 min. The dispersion behavior of the HA particles was studied as a function of the pH of the slurry and with the addition of two dispersing agents, labeled A and B (A = Calgon, or sodium hexametaphosphate, S. D. Fine Chemicals, Ltd., and B = Darvan C, or ammonium polymethacrylate, R. T. Vanderbilt Co., Inc., Norwalk, CT).

The dispersibility of HA powder in deionized water was evaluated by simple sedimentation experiments, using 12 wt% solids-loaded suspensions (2 g powder in 15 cm^3 deionized water) in the pH range 2–12, and as a function of the quantities of the two dispersing agents added (0–10 wt%, with respect to the HA powder). The particle/floc size distributions in the dispersion were determined using an X-ray sedimentation technique (Sedigraph Model 5100, Micromeritics Instrument Corp., Norcross, GA) for 5 wt% solids-loaded suspensions at different pH values. Similar suspensions containing 2 wt% of dispersing agent A or 3 wt% of dispersing agent B were also screened for particle-size distribution. The rheological behavior of 35–55 wt% solids-loaded HA slips was studied by measuring their viscosity and shear stress as a function of shear rates, with and without the addition of dispersing agents, using a rotational viscometer (Searle type, Viscotester VT-500, Haake, Karlsruhe, Germany). All of the results were correlated to optimize the conditions of best dispersibility of HA powder in deionized water.

(3) Slip Casting, Sintering, and Characterization of HA

The flow chart of the slip-casting process is given schematically in Fig. 1. The HA slips were prepared in deionized water, with optimum amounts of dispersing agents (achieved through the above experimental techniques); milled in polyethylene jars for 12–16 h, using Al_2O_3 milling media; and then cast into plaster molds, to obtain green bodies in simple shapes such as bars (40 mm × 8 mm × 8 mm) and disks (16 mm × 8 mm). The green bodies were air-sintered in the temperature range 1250°–1400°C for 2 h, in an SiC furnace. The green density, sintered density, linear shrinkage, and percentage weight loss were determined by weight and dimensional measurements. The apparent porosity was determined using Archimedes' method. The three-point flexural strengths of sintered rectangular bar specimens (30 mm × 6 mm × 5 mm) were measured, using a span width of 26 mm and a crosshead speed of 0.5 $mm \cdot min^{-1}$ (Universal Testing Machine, Model 6025, Instron Corp., High Wycombe, U.K.). The sintered disks, polished successively with 400 and 600 grit SiC emery and 2 μm Al_2O_3 slurry, were etched with 0.1*M* acetic acid for 2 min. The microstructural features of the polished, etched, and fractured surfaces were obtained by scanning electron microscopy (SEM; Model 440, Leo Electron Microscopy, Ltd., Cambridge, U.K.).

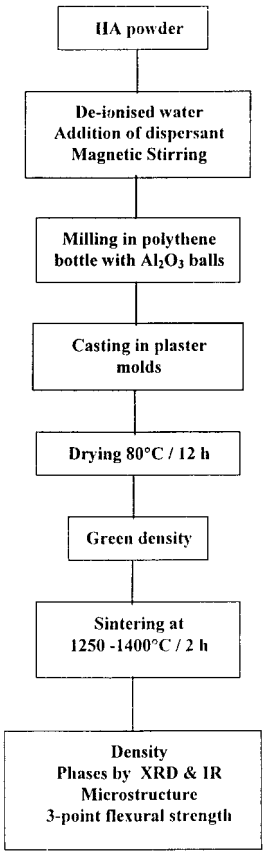

Fig. 1. Schematic flow chart, showing the processing route for obtaining slip-cast HA bodies.

III. Results and Discussion

(1) HA Powder Characterization

The HA powder prepared in the laboratory was pure single-phase HA, as shown by the X-ray diffractogram and the IR spectra of the powder, presented in Figs. 2(a) and (b), respectively. The reflections of the XRD spectrum in Fig. 2(a) agree very well with those of the standard XRD spectrum for hydroxyapatite,[21] and the absorption peaks of the IR spectra in Fig. 2(b) match those for pure HA reported by earlier workers.[12,20,22]

(2) Sedimentation Behavior of HA Slurry

The particle-settling characteristics of a 12 wt% slip left undisturbed for sedimenting in a glass tube were studied by

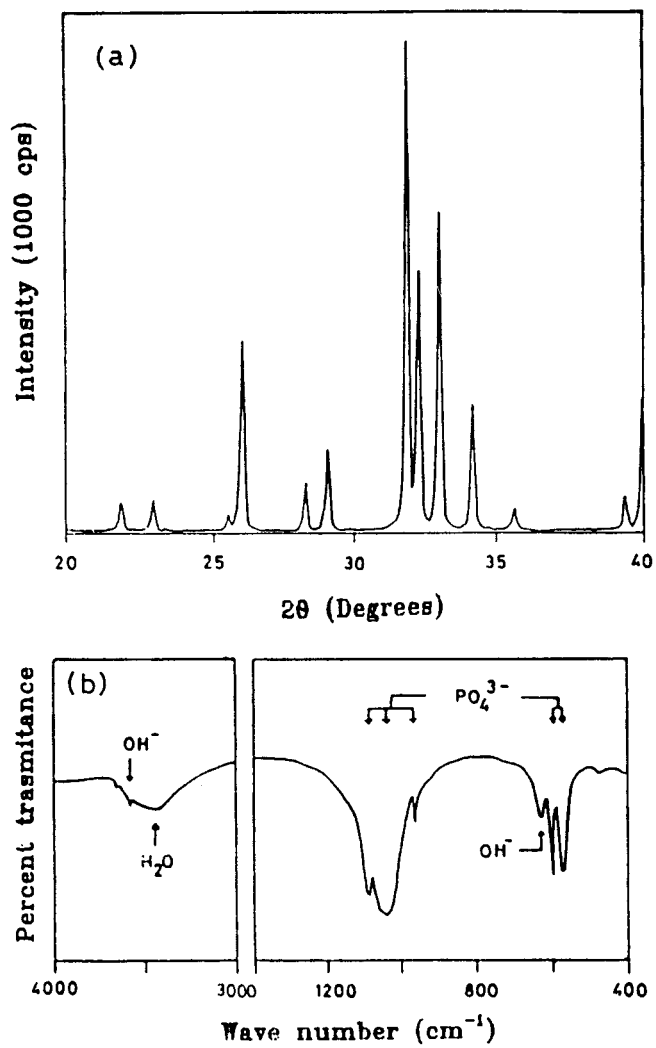

Fig. 2. (a) XRD and (b) IR spectra of synthesized HA powder.

measuring sedimentation heights as a function of time. The sedimentation heights measured after 1 h, shown in Fig. 3, reveal that the HA powder was highly flocculated in deionized water, with a very high settling rate. Variation of the pH had negligible effect on the dispersibility. This result is in good agreement with the results reported earlier by Toriyama *et al.*[15] The two dispersing agents used at different concentrations (up to 10 wt%, with respect to the HA powder) were not effective in breaking down the agglomerates at the normal low concentrations (<1 wt%) usually used for colloidal processing of other ceramic materials. However, higher concentrations of the dispersants (≥2–4 wt%) were able to yield well-dispersed slips with lower sedimenting rates, leading to much lower sediment heights. With dispersant A, the sedimentation heights were minimum when the dispersant was present in the range 2–5 wt%. At higher concentrations (>6 wt%) of dispersant A, the powders were again highly flocculated, resulting in increased sedimentation heights. In the case of dispersant B, the optimum dispersion was observed at dispersant concentrations >3 wt%.

The sedimentation behavior and stability of HA slips at various pH values and with the presence of dispersing agents, diagnosed by plotting the turbidity levels (total height of solids sedimented + particles under suspension below a clear supernatant liquid at the top) as a function of time, is shown in Fig. 4. Without the addition of dispersants, the HA particles were highly flocculated in the entire pH range studied (pH 2–12), and the particles started settling within 10 min of standing. The sedimentation was complete in ~1 h, attaining a plateau region in sedimentation heights (see Fig. 4). On the contrary, with dispersants A (2 wt%) and B (3 wt%), the highly dispersed HA particles were considerably stable, even after 10 h of standing. These results indicated that 2 wt% of dispersant A and 3 wt% of dispersant B could be the amounts to use for optimal dispersion of HA powder; hence, these concentrations were used in other characterization experiments.

The results of the sedimentation experiments were in accord with those reported by Toriyama *et al.*[15] and Terpstra *et al.*[19] Toriyama *et al.*[15] found that anionic polyacrylates were effective in stabilizing 10 vol% suspensions of mechanochemically synthesized HA when used in the concentration range 2–4 wt%, while Terpstra *et al.*[19] showed that commercial HA could be stabilized with ammonium polyacrylate as the dispersant at pH ≥10.

Polyacrylates have proved to be effective dispersing agents for both clay- and nonclay-based ceramics,[23,24] through an electrosteric mechanism of dispersing action. Similarly, various sodium polyphosphates have been used as effective deflocculating agents for many clay- and oxide-based ceramic systems.[25] The polyphosphates may act as either cationic (Na^+) or anionic (polyphosphate groups) dispersants, depending on the charge of the particle

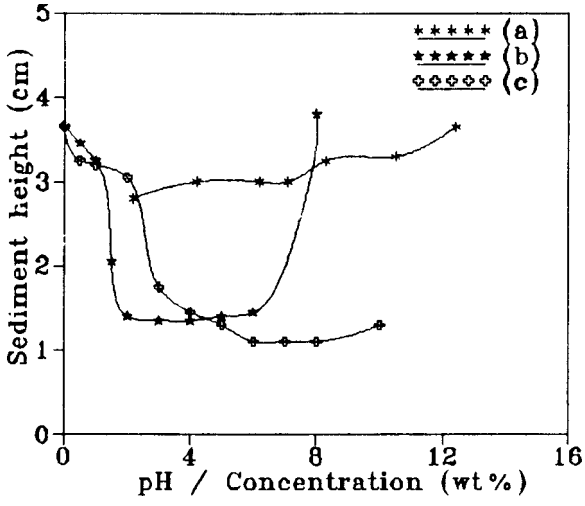

Fig. 3. Sedimentation heights for 12 wt% HA slips reached after 1 h in deionized water, as a function of (a) pH, (b) concentrations of dispersant A, and (c) concentrations of dispersant B.

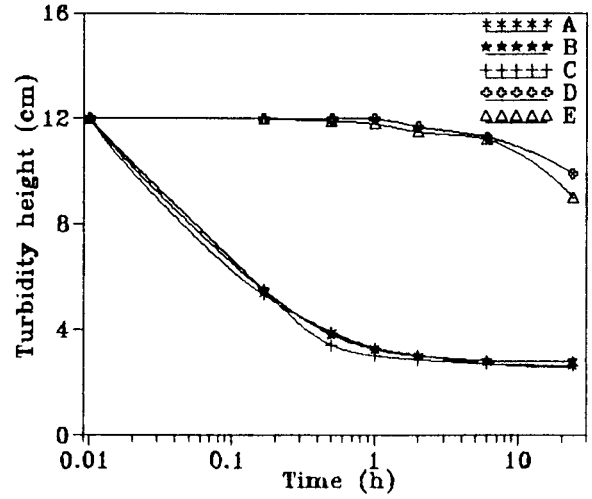

Fig. 4. Turbidity levels measured for free-standing HA slip, as a function of time, at (A) pH 11, (B) pH 8, and (C) pH 6, and for (D) 2 wt% of dispersant A and (E) 3 wt% of dispersant B.

surface. Because of their long chain structure, polyphosphates—e.g., sodium hexametaphosphate—provide a steric hindrance effect, along with the electrostatic dispersion effect.[25]

On dispersion into aqueous media, the HA particles could have on their surfaces various ions such as Ca^{2+}, $CaOH^+$, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, and $CaH_2PO_4^+$, depending on the dissolution and the hydrolytic reactions in solution, bringing into play a set of complex flocculating/deflocculating mechanisms. However, because HA slips could be dispersed and stabilized by the anionic polyelectrolytes, as well as by a polyphosphate, it can be concluded that the surface of HA is positively charged and the positive charge attributed to the specific adsorption of Ca^{2+} ions or to preferential dissolution of phosphate ions from the apatite surface.[26]

(3) Particle/Floc Size Distribution of HA

The particle/floc size distribution of HA powder, presented in Fig. 5, shows that the HA powders were highly agglomerated when dispersed in deionized water with a median diameter (d_{50}) of 23 μm and a narrow size distribution. On the contrary, the particles were well-dispersed in the presence of both dispersing agents, A (2%) and B (3%), as shown by the shift in the particle-size distribution curves to finer ranges with minimum values for particle sizes (dispersant A: d_{10} = 0.85 μm, d_{50} = 3.71 μm, d_{90} = 10.00 μm; dispersant B: d_{10} = 0.85 μm, d_{50} = 3.59 μm, d_{90} = 9.70 μm).

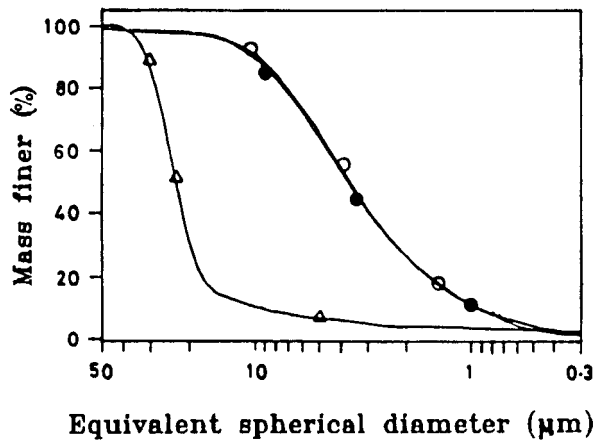

Fig. 5. Particle-size distribution for HA powder ((Δ) dispersant-free deionized water, (●) 2 wt% of dispersant A, (○) 3 wt% of dispersant B).

(4) Rheological Behavior of HA Slips

The viscosity and shear stress, measured as a function of shear rate, for 35 wt% (15 vol%) HA slips are presented in Fig. 6. The HA slip in deionized water was non-Newtonian, with high shear-thinning and slight thixotropic behavior, with a yield stress of ~5 Pa, characteristic of a highly flocculated condition of the slip. These results are similar to the findings of Liu[18] for 10–15 vol% solids-loaded HA slips, which exhibited a pseudoplastic shear-thinning behavior. The HA slips prepared with 2% of dispersant A and 3% of dispersant B showed Newtonian flow behavior, with a linear shear-stress-versus-shear-rate curve passing through the origin and a nonvariant viscosity with increasing shear rates, indicating the good dispersion of the powder particles in the medium.

The flow curves of shear stress and viscosity versus shear rate at different solids loadings (35–50 wt%) for HA slips containing 2% dispersant A (curves B–E), as well as for a 35 wt% HA slip without dispersing agent (curve A), are presented in Fig. 7. These results show that, with the presence of dispersing agent A, the HA slip was Newtonian, with considerably lower viscosity up to the solids-loading level of 45 wt% (20 vol%), whereas at 50 wt% (24 vol%), a shear-thinning behavior with a yield value of ~2 Pa occurred, indicating considerable flocculation of the powder particles. The viscosity values increased as a function of solids loading of the slip.

Similar flow curves for HA slips containing 3% of dispersant B, in Fig. 8 (curves B–E), show that the slip was near-Newtonian for 35 and 45 wt% solids loading. At 50 and 55 wt% solids loading, the slip showed a slight shear-thinning behavior for a lower range of shear rates (up to 600 S^{-1}), whereas at higher shear rates (>1000 S^{-1}), slight shear-thickening (dilatant) behavior was observed. This initial shear thinning, followed by a shear-thickening phenomenon, is a well-known characteristic of colloidally stable suspensions at higher solids loadings.[4,27] The initial shear thinning could be attributed to the increased tendency for flocculation, and the dilatancy at higher shear rates can be ascribed to shear-induced flocculation or transition from an ordered to a disordered structure as the interparticulate distances decrease with increasing solids loadings. The decreased viscosity and near-Newtonian flow behavior of the HA slips up to a solids loading of ~50 wt% (24 vol%) in the presence of the dispersing agents (curves B–E), as compared with higher viscosity and highly pseudoplastic shear-thinning flow behavior at a relatively lower solids loading of 35 wt% (20 vol%) without the addition of dispersing agents (curve A), indicate the enhanced dispersing effect of the two dispersing agents A and B, thereby correlating well with the results of sedimentation studies.

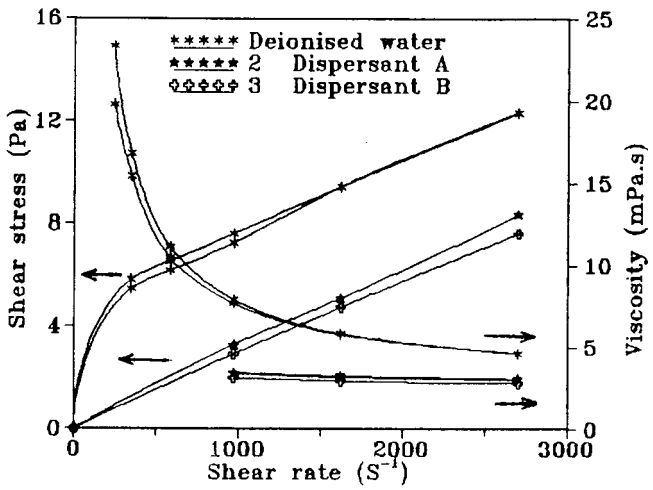

Fig. 6. Shear-stress-versus-shear-rate and viscosity-versus-shear-rate curves for 35 wt% HA slip in deionized water, with and without dispersing agents.

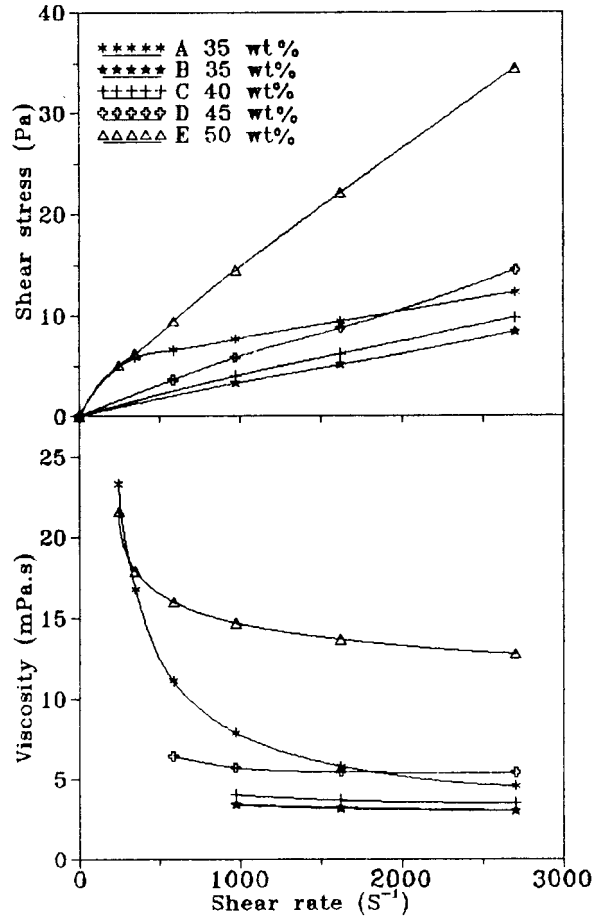

Fig. 7. Shear-stress-versus-shear-rate and viscosity-versus-shear-rate curves for HA slip (A) in deionized water at 35 wt% solids loading and (B)–(E) with 2 wt% of dispersant A at different solids loadings (35–50 wt%).

(5) Slip Casting of HA

The results of slurry-optimization experiments reveal that a well-dispersed HA slurry having near-Newtonian flow behavior could be prepared in deionized water up to a 50 wt% solids loading, using either of the two dispersing agents, A or B, in optimum amounts. The slip viscosity could be further decreased by breaking down the soft agglomerates through milling of the slip in polyethylene bottles with alumina milling media for various times, as indicated by the flow curves of viscosity versus shear rate for an HA slip made with 3 wt% of dispersant B before and after milling (12 h), shown in Fig. 9. The 55 wt% solids-loaded slip behaves as non-Newtonian, with slight shear thinning at lower shear rates (up to ~600 S^{-1}) and shear thickening at higher shear rates (>1000 S^{-1}) in the as-dispersed condition (before milling). On the contrary, the 60 wt% solids-loaded slip, after ball milling for ~12 h, shows relatively lower viscosity, as compared with a 55 wt% solids-loaded nonmilled slip, and a near-Newtonian flow behavior, with slight shear thinning, at lower shear rates.

By using optimum amounts of the dispersing agents (A = 2% and B = 3%), followed by milling for 5–15 h, a 60–67 wt% (32–39 vol%) solids-loaded HA slip could be prepared in deionized water and cast into plaster molds to produce green bodies having densities in the range 50%–58% of theoretical (3.16 $g \cdot cm^{-3}$ for HA). The typical casting conditions used and the green densities achieved are presented in Table I. The solids loading of the slip and the green density achieved were better than those reported by Toriyama *et al.*[15] and comparable to those reported by Galassi *et al.*[13] and Lelievre *et al.*[16] for HA slips, as well as to those reported by Nordstrom and Karlsson[14] for slurries made of TCP and $Ca(OH)_2$ mixtures. However, the highest green density, ~58% of theoretical in some cases, was considerably

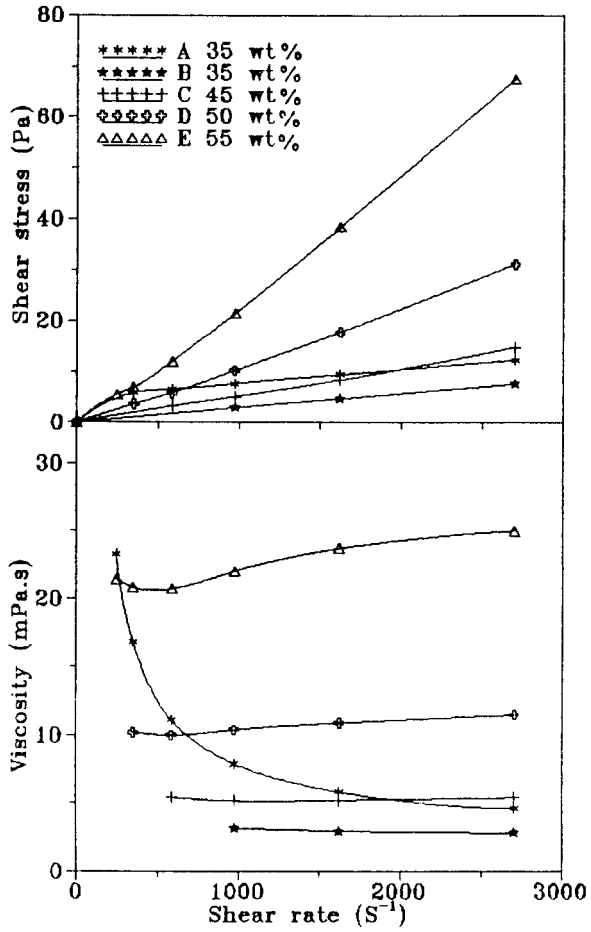

Fig. 8. Shear-stress-versus-shear-rate and viscosity-versus-shear-rate curves for HA slip (A) in deionized water at 35 wt% solids loading and (B)–(E) with 3 wt% of dispersant B at different solids loadings (35–55 wt%).

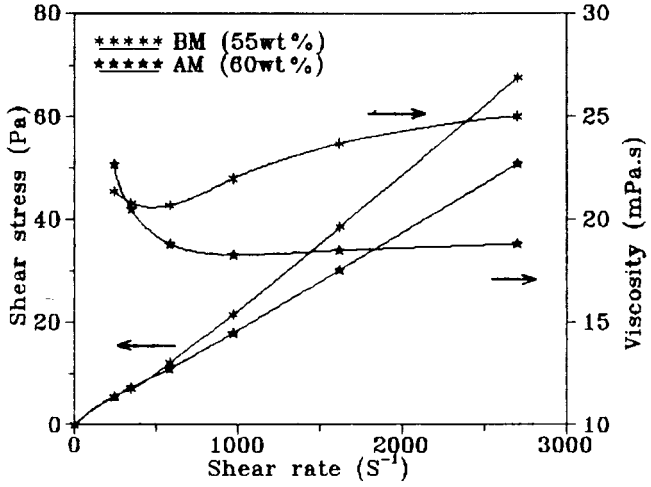

Fig. 9. Shear-stress-versus-shear-rate and viscosity-versus-shear-rate curves for HA slip with 3 wt% of dispersant B ((BM) 55 wt% solids loading before milling, (AM) 60 wt% solids loading after 12 h ball milling).

higher than the values reported in the literature. This variation in green density could be attributed to the critical effect of the presence of dispersing agents on the dispersability of HA particles.

(6) Sintering of HA

The slip-cast HA samples were sintered in the temperature range 1250°–1400°C for 2 h. Some select batch samples were sintered at 1350°C for 2 and 4 h. The typical density values of the sintered products are plotted versus the sintering temperatures in Fig. 10, for green bodies having 51% density. The increased densification observed as a function of temperature reached a maximum of ~93%–94% of theoretical at 1350°C, followed by a slight decrease at 1400°C. These results are in agreement with densification results achieved for uniaxially pressed pellets of the same HA powder,[28] as well as for those produced by solid-state reactions by other investigators.[10,12,17] However, the above density values (92%–94%) are slightly inferior to those reported (94%–99%) for HA prepared by other methods.[13–16,19] This difference is attributed to the coarser particles (d_{50} = 3.7 μm) of the present HA powder, as compared with those in the powders used by others, which generally were produced by precipitation and were finer, in the submicrometer (0.05–1.0 μm) range. XRD analysis of the slip-cast and sintered (1400°C) HA showed the phase stability of HA with a small amount (~2%) of α-TCP as the decomposition product.

Table I. Slip-Casting Conditions and Cast Properties of HA

Slip No.	Dispersant Type	Dispersant Amt. (wt%)	Solids loading (wt%)	pH	Milling time (h)	Green density ($g \cdot cm^{-3}$)	Green density (%)†
1	A	2.0	55	12	5	1.249	39.5
2	A	2.0	64	11	15	1.563	49.5
3	A	2.0	67	11.5	13	1.601	50.7
4	A	1.8	65	10.5	17	1.606	50.8
5	B		46	8.9	13	1.358	43.0
6	B	3.6	61	9.6	5	1.611	51.0
7	B	3.8	65	9.3	6	1.695	53.6
8	B	3.0	60	8.3	11	1.616	51.2
9	B	4.2	67		9	1.608	50.9
10	B		64	8.5	13	1.851	58.6
11	B		60	8.6	18	1.840	58.2

†Percentage of theoretical density (density of HA = 3.16 $gm \cdot cm^{-3}$).

(7) Mechanical and Microstructural Characterization of Slip-Cast HA

The typical three-point flexural strength values of slip-cast sintered HA samples are presented in Table II, together with their green and sintered densities and apparent porosities. Scanning electron micrographs of the polished and etched surfaces of the sintered HA and of the fractured surfaces of the slip-cast green and sintered bodies are presented in Figs. 11(a)–(d), respectively. The flexural strength values (modulus of rupture (MOR) = 37–58 MPa) are a function of the final density of the sintered specimens. The strength values obtained for slip-cast HA in the

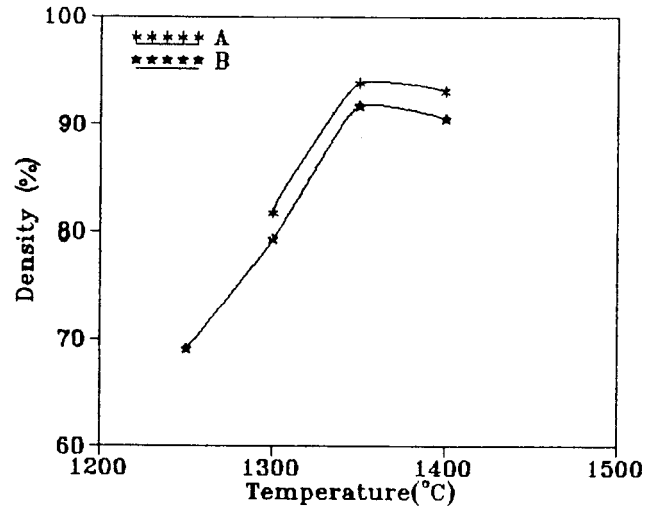

Fig. 10. Sintered density of slip-cast HA, as a function of sintering temperature, for (A) dispersant A and (B) dispersant B.

Table II. Characteristics of Slip-Cast Sintered HA Products

Sample identity	Green density ($g \cdot cm^{-3}$)	Green density (%)	Sintered density ($g \cdot cm^{-3}$)	Sintered density (%)	Apparent porosity (%)	MOR† (MPa)
H1	1.6106	51.0	2.703	85.5	7.1	37
H2	1.6162	51.2	2.887	91.4	4.2	59
H3	1.5664	49.6	2.831	89.6	5.0	56

†Modulus of rupture (three-point bend test data).

present study were slightly lower than the best values presented in the literature. This difference stems from the lower density (82%–92%) values of the sintered product and is also attributable to the relatively coarser initial grain sizes of the precursor powder, resulting from the high temperatures of solid-state reaction. However, these strength values are extremely promising in comparison with the widely scattered and lower values obtained by Wang and Chaki (14–15 MPa),[29] Juang and Hon (25–40 MPa),[30] and Puajindanetr *et al.* (25–65 ± 12 MPa).[31]

The SEM image in Fig. 11(a) shows a homogeneous dispersion of fine particles in the green body, which can be attributed mainly to the optimal dispersion conditions of HA powders in aqueous media afforded by the addition of dispersing agents. The sizes of the HA particles in the image are comparable to the particle-size distribution analysis ($d_{10} = 0.85$ μm, $d_{50} = 3.7$ μm, $d_{90} = 10$ μm) presented in Fig. 5. The morphology of the polished and etched surface, as well as that of the fractured surface, of the slip-cast and sintered HA, shown in Figs. 11(b)–(d), correlates very well with those obtained for the uniaxially pressed and sintered HA[28] and with those presented by other workers.[13,16,30,32–37] Figures 11(b) and (c) show the intergranular microporosities (1–2 μm) uniformly distributed throughout the body and a uniform grain-size distribution of 3–8 μm. Coalescence of the grains results in densification, as observed in Figs. 11(c) and (d), and the fracture phenomena observed are both intragranular and intergranular. A comparison of Figs. 11(c) and (d) reveals that some grain growth occurs with sintering at the higher temperature of 1400°C (Fig. 11(d)), as compared with sintering at 1350°C (Fig. 11(c)).

IV. Conclusion

The HA powders synthesized by a high-temperature solid-state reaction between TCP and $Ca(OH)_2$ were highly agglomerated/flocculated when dispersed in an aqueous medium. Alteration of the pH of the medium had no effect on the dispersion of the HA powder. Two dispersing agents, studied for their influence on the deagglomeration and dispersion of HA powders in aqueous media, were effective only when used at higher concentrations, in the range of 2–4 wt% of HA. A well-dispersed slip with optimum amounts of dispersing agents displayed near-Newtonian flow behavior up to a solids loading of 45 wt% and non-Newtonian behavior for solids loadings of >50 wt%. With the use of optimum amounts of dispersing agents and conditioning by ball milling, HA slips having 60–67 wt% of solids loading could be slip cast into compacts having 50%–58% green density, which, in turn, sintered to 90%–93% density in the temperature range 1300°–1400°C. The slip-cast and sintered HA specimens exhibited a promising mechanical strength (three-point flexural strength) of 40–60 MPa, indicating that these products could be useful for biomechanical applications.

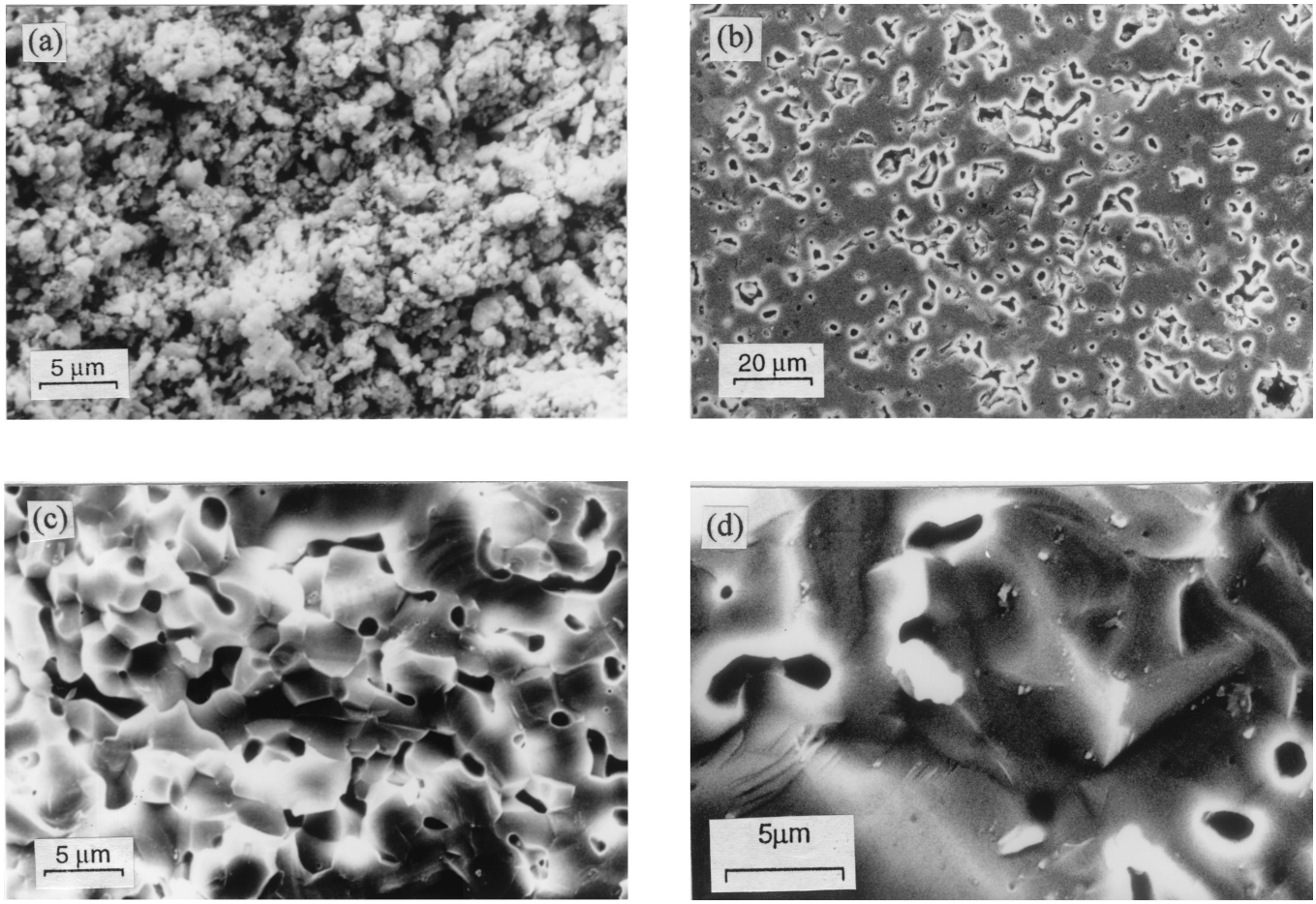

Fig. 11. SEM images of (a) fractured surface of HA slip-cast green body, (b) polished and etched surface of HA sintered at 1400°C for 2 h, (c) fractured surface of HA sintered at 1350°C for 2 h, and (d) fractured surface of HA sintered at 1400°C for 2 h.

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References

[1]P. Rado, "Slip-Casting of Non-Clay Ceramics," *Interceram.*, **36** [4] 34–37 (1987).
[2]P. E. Rempes, B. C. Weber, and M. A. Schwartz, "Slip Casting of Metals, Ceramics, and Cermets," *Am. Ceram. Soc. Bull.*, **37** [7] 334–39 (1958).
[3]R. Herrmann, "Slip Casting in Practice"; Sect. 4.2.1 in *Ceramic Monographs*, Handbook of Ceramics, Vol. 1 (Supplement to *Interceram.*, **38** [4/5] Suppl. 1–6 (1989)).
[4]R. Ramachandra Rao, H. N. Roopa, and T. S. Kannan, "Dispersion, Slip Casting and Reaction Nitridation of Silicon–Silicon Carbide Mixtures," *J. Eur. Ceram. Soc.*, **19** [12] 2145–53 (1999).
[5]F. F. Lange, "Powder Processing Science and Technology for Increased Reliability," *J. Am. Ceram. Soc.*, **72** [1] 3–15 (1989).
[6]Y. Hirata, "Theoretical Aspects of Colloidal Processing," *Ceram. Int.*, **23** [1] 93–98 (1997).
[7]L. L. Hench, "Bioceramics: From Concept to Clinic," *J. Am. Ceram. Soc.*, **74** [7] 1487–510 (1991).
[8]C. Lavernia and J. M. Schoenung, "Calcium Phosphate Ceramics as Bone Substitutes," *Am. Ceram. Soc. Bull.*, **70** [1] 95–100 (1991).
[9]W. Cao and L. L. Hench, "Bioactive Materials," *Ceram. Int.*, **22** [6] 493–507 (1996).
[10]T. S. B. Narasaraju and D. E. Phebe, "Review: Some Physicochemical Aspects of Hydroxyapatite," *J. Mater. Sci.*, **31** [1] 1–21 (1996).
[11]G. Willmann, "Medical Grade Hydroxyapatite: State of the Art," *Br. Ceram. Trans.*, **95** [5] 212–16 (1996).
[12]R. Z. LeGeros and J. P. Legeros, "Dense Hydroxyapatite"; pp.139–80 in *An Introduction to Bioceramics*, Advanced Series in Ceramics, Vol. 1. Edited by L. L. Hench and J. Wilson. World Scientific, Singapore, Republic of Singapore, 1993.
[13]C. Galassi, E. Roncari, A. Ravaglioli, and R. Martinetti, "Slip Casting of Hydroxyapatite for Bone Replacement"; pp. 3.43–3.47 in Proceedings of the First European Ceramic Society Conference, Euro-Ceramics, Vol. 3, *Engineering Ceramics, including Bioceramics.* Edited by G. de With, R. A. Terpstra, and R. Metselaar. Elsevier Applied Science, London, U.K., 1989.
[14]E. G. Nordstrom and K. H. Karlsson, "Slip-Cast Apatite Ceramics," *Am. Ceram. Soc. Bull.*, **69** [5] 824–27 (1990).
[15]M. Toriyama, A. Ravaglioli, A. Krajewski, C. Galassi, E. Roncari, and A. Piancastelli, "Slip Casting of Mechanochemically Synthesised Hydroxyapatite," *J. Mater. Sci.*, **30** [12] 3216–21 (1995).
[16]F. Lelievre, D. Bernache-Assollant, and T. Chartier, "Influence of Powder Characteristics on the Rheological Behaviour of Hydroxyapatite Slurries," *J. Mater. Sci.: Mater. Med.*, **7** [8] 489–94 (1996).
[17]I. H. Arita, V. M. Castano, and D. S. Wilkinson, "Synthesis and Processing of Hydroxyapatite Ceramic Tapes with Controlled Porosity," *J. Mater. Sci.: Mater. Med.*, **6** [1] 19–23 (1995).
[18]D.-M. Liu, "Preparation and Characterisation of Porous Hydroxyapatite Bioceramic via a Slip Casting Route," *Ceram. Int.*, **24** [6] 441–46 (1998).
[19]R. A. Terpstra, J. C. T. van der Heijde, P. Swaanen, X. Zhang, and G. Gubbels, "Slip Casting of Hydroxyapatite Ceramics"; pp. 61–66 in Proceedings of the Third European Ceramic Society Conference, Euro-Ceramics, Vol. 3, *Engineering Ceramics.* Edited by P. Duran and J. F. Fernandez. Faenza Editrice Iberica S.L., San Vicente, Spain, 1993.
[20]R. Ramachandra Rao, H. N. Roopa, and T. S. Kannan, "Solid State Synthesis and Thermal Stability of HAP and HAP–β-TCP Composite Ceramic Powders," *J. Mater. Sci.: Mater. Med.*, **8** [8] 511–18 (1997).
[21]Powder Diffraction File Card No. 9-432, Joint Committee on Powder Diffraction Standards (JCPDS), Swarthmore, PA (now International Centre for Diffraction Data, Newtown, PA), 1967.
[22]A. Slosarczyk, C. Paluszkiewicz, M. Gawlicki, and Z. Paszkiewicz, "The FTIR Spectroscopy and QXRD Studies of Calcium Phosphate Based Materials Produced from Powder Precursors with Different Ca/P Ratios," *Ceram. Int.*, **23** [4] 297–304 (1997).
[23]A. B. Corradi, T. Manfredini, G. C. Pellacani, and P. Pozzi, "Deflocculation of Concentrated Aqueous Clay Suspensions with Sodium Polymethacrylates," *J. Am. Ceram. Soc.*, **77** [2] 509–13 (1994).
[24]S. Baklouti, C. Pagnoux, T. Chartier, and J. F. Baumard, "Processing of Aqueous α-Al_2O_3, α-SiO_2, and α-SiC Suspensions with Polyelectrolytes," *J. Eur. Ceram. Soc.*, **17** [12] 1387–92 (1997).
[25]J. Faison and R. A. Haber, "Use of Polyphosphates as Deflocculants of Alumina," *Ceram. Eng. Sci. Proc.*, **12** [1–2] 106–15 (1991).
[26]P. Somasundaran, "Zeta Potential of Apatite in Aqueous Solutions and Its Change during Equilibration," *J. Colloid Interface Sci.*, **27** [4] 659–66 (1968).
[27]L. Bergstrom, "Rheology of Concentrated Suspensions"; pp. 193–244 in *Surface and Colloid Chemistry in Advanced Ceramics Processing.* Edited by R. J. Pugh and L. Bergstrom. Marcel Dekker, New York, 1994.
[28]R. Ramachandra Rao, H. N. Roopa, and T. S. Kannan, "Synthesis of Pure HAP and HAP–β-TCP Biphasic Mixtures by Solid State Reaction," *Trans. Indian Ceram. Soc.*, **57** [3] 73–76 (1998).
[29]P. E. Wang and T. K. Chaki, "Sintering Behaviour and Mechanical Properties of Hydroxyapatite and Dicalcium Phosphate," *J. Mater. Sci.: Mater. Med.*, **4** [2] 150–58 (1993).
[30]H.-Y. Juang and M.-H. Hon, "The Effect of Calcination Temperature on the Behaviour of HA Powder for Injection Moulding," *Ceram. Int.*, **23** [5] 383–87 (1997).
[31]S. Puajindaneter, S. M. Best, and W. Bonfield, "Characterisation and Sintering of Precipitated Hydroxyapatite," *Br. Ceram. Trans.*, **93** [3] 96–99 (1994).
[32]A. Tampieri, G. Celotti, F. Szontagh, and E. Landi, "Sintering and Characterization of HA and TCP Bioceramics with Control of Their Strength and Phase Purity," *J. Mater. Sci.: Mater. Med.*, **8** [1] 29–37 (1997).
[33]J. Li and L. Hermansson, "Mechanical Evaluation of Hot Isostatically Pressed Hydroxyapatite," *Interceram.*, **39** [2] 13–15 (1990).
[34]S. Best and W. Bonfield, "Processing Behaviour of Hydroxyapatite Powders with Contrasting Morphology," *J. Mater. Sci.: Mater. Med.*, **5** [8] 516–21 (1994).
[35]M. A. Fanovich and J. M. Portolopez, "Influence of Temperature and Additives on the Microstructure and Sintering Behaviour of Hydroxyapatites with Different Ca/P Ratios," *J. Mater. Sci.: Mater. Med.*, **9** [1] 53–60 (1998).
[36]A. Osaka, Y. Miura, K. Takeuchi, M. Asada, and K. Takahashi, "Calcium Apatite Prepared from Calcium Hydroxide and Orthophosphoric Acid," *J. Mater. Sci.: Mater. Med.*, **2** [1] 51–55 (1991).
[37]Y. Fang, D. K. Agrawal, D. M. Roy, and R. Roy, "Microwave Sintering of Hydroxyapatite Ceramics," *J. Mater. Res.*, **9** [1] 180–87 (1994). □